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(54) Title: SILICONE METHACRYLATE HYDROGELS FOR CONTACT LENSES

(57) Abstract

Contact lens polymers, i.e. polymers having optical and mechanical properties suitable for use in contact lenses, consisting essentially of copolymers of siloxane monomethacrylates and dimethacrylates, and copolymers of such materials with vinyl pyrrolidinone and pentafluorostyrene and also with methyl methacrylate and methacrylic acid, as exemplary of classes of monomers which may be included in the lens polymer system.

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SILICONE METHACRYLATE HYDROGELS FOR CONTACT LENSES

Technical Field

This invention relates to optical contact lenses and, more particularly, to optical contact lenses, lens materials and optical quality copolymers having qualities rendering them suitable for use in optical contact lenses, e.g. clarity, machinability, strength and durability, and which also possess unique and vastly improved oxygen permeability and wettability.

The lenses of this invention and the lens polymers, i.e., copolymer systems which possess qualities rendering them suitable for use in optical contact lenses, are copolymers of silicone monomers and prepolymers, and acrylate and methacrylate monomers, and include substituents which vastly improve wettability and oxygen permeability such as pentafluorostyrene,and vinyl pyrrolidinone to improve wettability.

Background Art

The prior art teaches the use of many different polymeric materials in contact lenses. However, although these polymers possess the optical clarity necessary for corrective lenses, they suffer from other characteristics which reduce their potential utility.

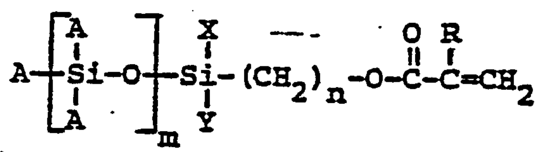
Polymethylmethacrylate is rigid and durable but relatively impermeable to oxygen. The hydrogel materials based on hydrophilic polymers such as polyhydroxyethylmethacrylate are soft and have poor durability. In addition, they provide an environment which is favorable for bacterial growth and are only moderately impermeable to oxygen.

Silicone rubber is soft and resilient and is highly permeable to oxygen. However, due to the low strength of polysiloxanes, a filler which increases the refractive index of the mixture, must be added to improve the durability.

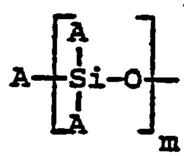
Further, the precision machining and polishing which is necessary in the fabrication of a corrective contact lens is extremely difficult with the elastomeric silicone rubbers.

Accordingly, it would be highly desirable to provide a polymeric material suitable for use in fabricating contact lenses having increased oxygen permeability, improved mechanical strength, and which is sufficiently rigid to permit precision machining and polishing. I have now discovered novel copolymer materials which possess these properties.

The prior art also teaches copolymers prepared by copolymerizing a polysiloxanylalkyl ester of acrylic or methacrylic acid with an alkanol ester of acrylic or methacrylic acid. In these copolymers the polysiloxanylalkyl ester monomer has the structural formula



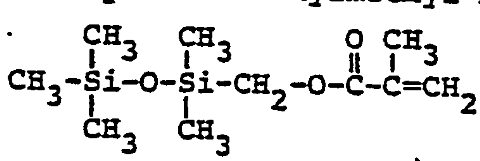
wherein X and Y are selected from the class consisting of C_1-C_5 alkyl groups, phenyl groups and Z groups; Z is a group of the structure



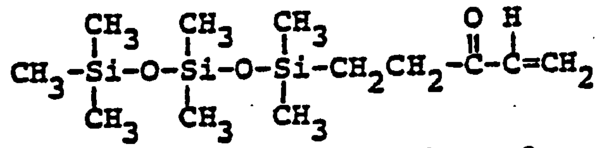
A is selected from the class consisting of C_1-C_5 alkyl groups and phenyl groups; R is selected from the class consisting of methyl groups and hydrogen; m is an integer from one to five; and n is an integer from one to three.

In the alkanol ester comonomers, the alkyl group contains from 1 to 20 carbon atoms. The polysiloxanylalkyl ester comonoers in these copolymers were:

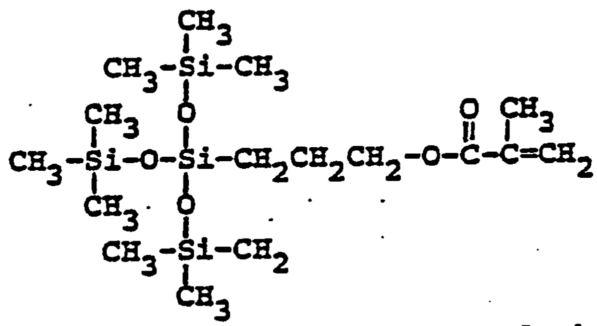
pentamethyldisiloxanylmethyl methacrylate



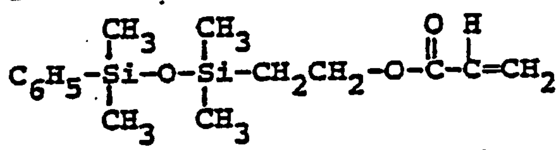
heptamethyltrisiloxanylethyl acrylate



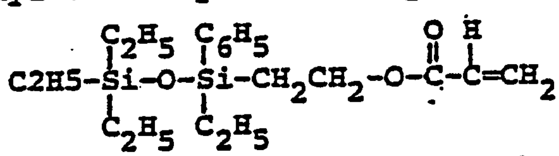
tris(trimethylsiloxy-γ-methacryloxypropylsilane



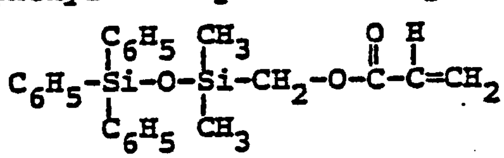
phenyltetramethyldisiloxanylethyl acrylate



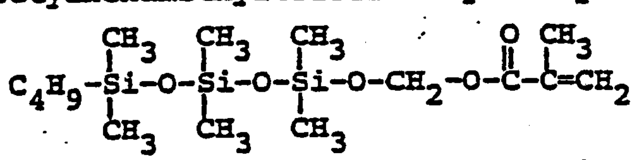
phenyltetraethyldisiloxanylether methacrylate



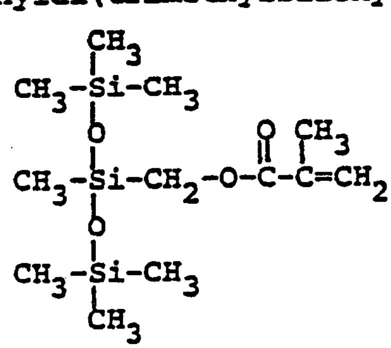
triphenyldimethyldisiloxanylmethyl acrylate



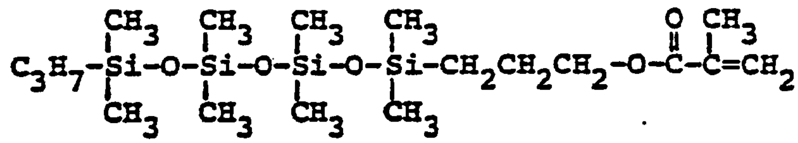
isobutylhexamethyltrisiloxanylmethyl methacrylate



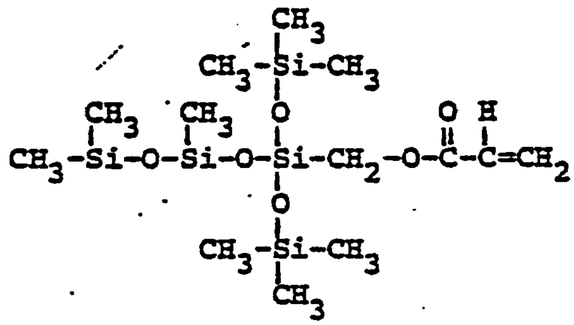
methyldi(trimethylsiloxy)-methacryloxymethylsilane



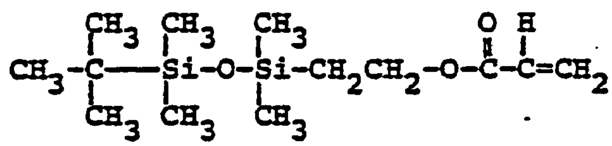
n-propyloctamethyltetrasiloxanylpropyl methacrylate



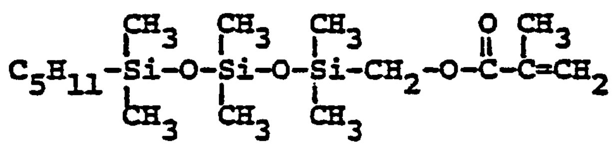
pentamethyldi(trimethylsiloxy)-acryloxymethylsilane



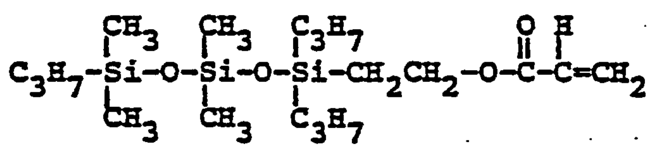
t-butyltetramethyldisiloxanylethyl acrylate



n-pentylhexamethyltrisiloxanylmethyl methacrylate



tri-i-propyltetramethyltrisiloxanylethyl acrylate



Representative alkanol ester comonomers included:

methyl acrylate and methacrylate
ethyl acrylate and methacrylate
propyl acrylate and methacrylate
isopropyl acrylate and methacrylate
butyl acrylate and methacrylate
amyl acrylate and methacrylate
hexyl acrylate and methacrylate
heptyl acrylate and methacrylate
octyl acrylate and methacrylate
2-ethylhexyl acrylate and methacrylate

nonyl acrylate and methacrylate
decyl acrylate and methacrylate
undecyl acrylate and methacrylate
lauryl acrylate and methacrylate
cetyl acrylate and methacrylate
octadecyl acrylate and methacrylate

These copolymers of the prior art comprise about 10-60 parts by weight of one or more of the polysiloxanylalkyl ester monomers copolymerized with about 49-90 parts by weight of one or more of the alkanol ester comonomers.

These prior art copolymers were prepared by contacting the mixture of comonomers with a free radical generating polymerization initiator of the type commonly used in polymerizing ethylenically unsaturated compounds. Representative free radical polymerization initiators include:

acetyl peroxide
lauroyl peroxide
decanoyl peroxide
caprylyl peroxide
benzoyl peroxide
tertiarybutyl peroxypivalate
diisopropyl peroxycarbonate
tertiarybutyl peroctoate
a, a'-azobisisobutyronitrile

Conventional polymerization techniques were employed to produce these copolymers. The comonomer mixture containing between about 0.05-2% by weight of the free radical initiator is heated to a temperature between 30°C.-100°C., preferably below 70°C., to initiate and complete the polymerization. The polymerization can be carried out directly in a c ntact lens mold to form a l ns generally having the desired configuration. Alternatively, the polymerization mixture can be heated

in a suitabl mold or container to form discs, rods or sheets which can then be machined to the desired shape using conventional equipment and procedures employed for fabricating lenses from polymethyl methacrylate. The temperature is preferably maintained below 70°C. in order to minimize the formation of bubbles in the copolymer. Instead of employing the bulk polymerization techniques described above, one can employ solution, emulsion or suspension polymerization to prepare the novel copolymers, using techniques conventionally used in the preparation of polymers from ethylenically unsaturated monomers. The copolymer thus produced may be extruded, pressed or molded into rods, sheets or other convenient shapes which are then machined to produce the contact lenses.

The aforementioned silicone-acrylate copolymers, described more fully in U.S. Patent No. 3,808,178, had increased oxygen permeability as compared with acrylic polymers and increased wettability as compared with silicone rubber.

Improved wettability was imparted to the copolymer by the addition of from about 0.1% to about 10% by weight of one or more hydrophilic monomers to the copolymerization mixture. Such monomers include hydroxyalkyl acrylates and methacrylates wherein the alkyl group contains 1 to 4 carbon atoms, acrylic and methacrylic acid, acrylamide, methacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, glycidyl acrylate and methacrylate and N-vinylpyrrolidone. Alternatively, the wettability of the surface of contact lenses made from these copolymers was improved by the application of a wetting agent such as, for example, a dilute aqueous solution of alkyldimethylbenzylammonium chloride, by exposure of the surface to a corona discharge or by chemical treatment of the surface with a strong oxidizing agent such as nitric acid.

The rigidity of the contact lenses prepared from such copolymers could be varied by changing the ratio of comonomers and/or their chemical composition. Contact lenses prepared from acrylate monomers are more flexible than those prepared from methacrylate monomers. A copolymer of a polysiloxanylalkyl methacrylate and an alkyl methacrylate fabricated into a contact lens is more rigid than a lens prepared from the copolymer of the corresponding acrylates. The lower the alkyl methacrylate content of the copolymer the more flexible the contact lens prepared therefrom.

The rigidity of a contact lens prepared from the aforesaid materials could be increased by the incorporation into the copolymer composition of 0.01% to about 2% by weight of a crosslinking monomer such as a polyol dimethacrylate or diacrylate or a polyol acrylic ester of higher functionality, for example, ethylene glycol dimethacrylate, butylene glycol dimethacrylate, neopentyl glycol diacrylate and pentacrythritol triacrylate or tetra-acrylate.

The refractive index of polymethylmethacrylate, the polymer most widely used in the fabrication of contact lenses, is 1.49. The refractive indices of the copolymers referred to above could be varied between 1.35 and 1.50 by varying the ratio and nature of the comonomers. In general, increasing the polysiloxanyl monomer content of the copolymer will decrease its refractive index. The nature of the substituents on the silicon atoms of the polysiloxanyl monomer also importantly affects the refractive index of the copolymer. Lower straight chain alkyl substituents produce copolymers of lower refractive index while polysiloxanyl monomers having phenyl substituents on the silicon atoms yield copolymers having a higher refractive index. (See U.S. Patent 3,808,178)

Statement of the Invention

The present invention is an improvement over the prior art lenses and comprises lenses, lens polymers and methods of preparing contact lenses and contact lens polymers of specific and unique copolymeric composition having unique and surprising advantages.

In one facet, the invention features copolymers of acrylate and siloxane monomers in which each end of the siloxane is capped with an acrylic or methacrylic acid moiety, the polymer comprising a poly(diacrylic siloxane).

In another facet, the invention features particular copolymers of monoacrylic siloxane, as described in the aforesaid prior art patent, and diacrylic siloxane, such copolymers possessing very much improved and unexpected advantages over the prior art and also possessing properties not predictable from known characteristics of prior art polymer and copolymer systems.

In an additional facet, the invention features particular copolymers which include a pentfluorostyrene moiety which vastly improves oxygen permeability and yet possess highly advantageous characteristics as a lens polymer.

Still another and very important facet of the invention is a particular set of copolymers of wettable poly(hydroxyalkyl methacrylate-siloxane-methacrylate-n-vinyl pyrrolidinone) which have extremely high wettability and yet are clear and otherwise suitable as lens polymers.

Lenses made of the aforementioned copolymer systems and methods of forming the same are also facets of this invention.

The term "lens polymer" is commonly and widely used in the contact lens industry and is used herein to mean a polymer or copolymer material which possesses physical and optical characteristics which render the material suitable for being formed into and used as a lens, and

in this particular application, as a contact lens. Such material must be clear, have an adequately high refractive index, i.e., above about 1.25 and generally up to about 1.5, the higher the refractive index the more correction availability, and must also be firm and rigid enough to be machined and polished, and tough enough to be handled and worn as a contact lens. These characteristics of contact lens polymers are well and generally known in the industry and need not be quantified. Indeed, toughness and handleability are not capable of any meaningful quantitative definition, though hardness and resilience are included in the general concept of toughness.

In a more specific sense the present invention includes lenses formed from a lens polymer consisting essentially of the solid polymerization product of comonomers consisting essentially of:

(a) from about 5 weight percent to about 99 weight percent silicone monoacrylate or methacrylate having the formula:

$$R_2-\overset{\displaystyle R_4}{\underset{\displaystyle R_5}{\overset{|}{\underset{|}{Si}}}}-R_1-\overset{\displaystyle R_6}{\underset{\displaystyle R_7}{\overset{|}{\underset{|}{Si}}}}-R_3$$

wherein:

R_1 is a group selected from $-O-$; $-\overset{\displaystyle R_8}{\underset{\displaystyle R_9}{\overset{|}{\underset{|}{Si}}}}-O-$; or $-\overset{\displaystyle R_{10}}{\underset{\displaystyle R_{11}}{\overset{|}{\underset{|}{Si}}}}-O-\overset{\displaystyle R_{12}}{\underset{\displaystyle R_{13}}{\overset{|}{\underset{|}{Si}}}}-O-$;

R_2 is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$;

R_3 is a group selected from

$$CH_2=\underset{\displaystyle C_mH_{2m+1}}{\underset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_n-;\quad \text{or}\quad CH_2=CH-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_n-;$$

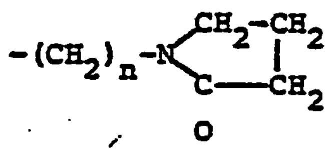
m being a positive integer from 1 to 3;

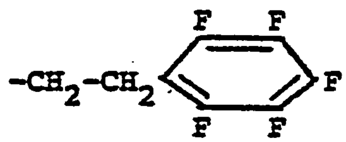
R_4 through R_{13}, inclusive, each is a group selected from

$$C_nH_{2n+1};\ -C_6H_5;\ \text{or}\ \left[-O-Si-(CH_2)\right]_n-R_{14};$$

R_{14} is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$ or $\left[-O-Si-(CH_2)_2\right]_n-R_{15}$

R_{15} is a group selected from $-C_nH_{2n+1}$; C_6H_5;

 or

 ;

wherein when any of R_4 through R_{13} is other than $-CH_3$, then the substituents R on adjacent siloxane groups,

$$-O-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-$$

are $-C_nH_{2n+1}$ or $-C_6H_5$ and wherein n is a positive integer from 1 to 5; and

(b) from about 1 weight percent to about 95 weight percent silicone diacrylate or dimethacrylate having the formula

$$R_3-\overset{\displaystyle R_4}{\underset{\displaystyle R_5}{Si}}-R_1-\overset{\displaystyle R_6}{\underset{\displaystyle R_7}{Si}}-R_3,$$

wherein:

R_1 is a group selected from $-O-$; $-\overset{\displaystyle R_8}{\underset{\displaystyle R_9}{Si}}-O-$; or $-\overset{\displaystyle R_{10}}{\underset{\displaystyle R_{11}}{Si}}-O-\overset{\displaystyle R_{12}}{\underset{\displaystyle R_{13}}{Si}}-O-$;

R_3 and R_3, each is a group selected from

$$CH_2=\underset{\displaystyle C_mH_{2m+1}}{C}-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_n-;\text{ or } CH_2=CH-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_n-;$$

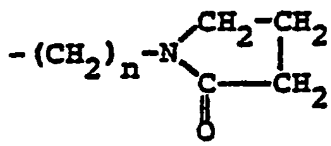
m being a positive integer from 1 to 3;

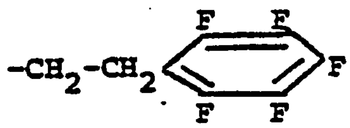
R_4 through R_{13}, inclusive, each is a group selected from C_nH_{2n+1}; $-C_6H_5$; or $\left[-O-Si-(CH_2)\right]_n-R_{14}$;

R_{14} is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$ or

$$\left[-O-Si-(CH_2)_2\right]_n-R_{15}$$

R_{15} is a group selected from $-C_nH_{2+1}$; $-C_6H_5$;

 or

 ;

and wherein when any of R_4 through R_{13} is other than $-CH_3$, then the substituents R on adjacent siloxane groups,

$$-O-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-$$

are $-C_nH_{2n+1}$ or $-C_6H_5$
and wherein n is a positive integer from 1 to 5.

In a still more specific sense the present invention includes lens polymers which have physical and optical properties suitable for being formed into contact lenses consisting essentially of the polymerization product of the following comonomers:

(a) from about 5 to about 99 percent by weight of a silicone monoacrylate or monomethacrylate having the formula

$$R_2-\overset{\displaystyle R_4}{\underset{\displaystyle R_5}{Si}}-R_1-\overset{\displaystyle R_6}{\underset{\displaystyle R_7}{Si}}-R_3$$

wherein:

R_1 is a group selected from $-O-$; $-\overset{\displaystyle R_8}{\underset{\displaystyle R_9}{Si}}-O-$; or $-\overset{\displaystyle R_{10}}{\underset{\displaystyle R_{11}}{Si}}-O-\overset{\displaystyle R_{12}}{\underset{\displaystyle R_{13}}{Si}}-O$;

R_2 is a group selected from $-C_nH_{2n+1}$ or $-C_6H_5$.

R_3 is a group selected from

$$CH_2=\underset{\displaystyle C_mH_{2m+1}}{C}-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_n-;\text{ or }CH_2=CH-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_n-;$$

m being a positive integer from 1 to 3;

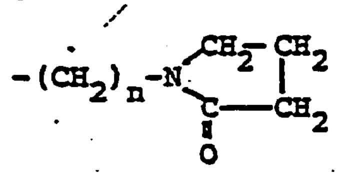
R_4 through R_{13}, inclusive, each is a group selected from

$$-CH_3;\ -C_6H_5;\ \text{or}\ \left[-O-Si-(CH_2)\right]_n-R_{14};$$

R_{14} is a group selected from $-CH_3$; $-C_6H_5$ or

$$\left[-O-Si-(CH_2)_2\right]_n-R_{15}$$

R_{15} is a group selected from $-CH_3$; $-C_6H_5$;



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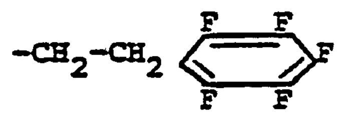


;

and wherein when any of R_4 through R_{13} is other than $-CH_3$, then the substituents R on adjacent siloxane groups,

$$-O-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-\quad ---$$

are $-C_2H_{2n+1}$ or $-C_6H_5$;

and wherein n is a positive integer from 1 to 3; and

(b) from about 1 to about 95 percent by weight of a silicone diacrylate or dimethacrylate having the formula:

$$R_3-\underset{R_5}{\overset{R_4}{\underset{|}{\overset{|}{Si}}}}-R_1-\underset{R_7}{\overset{R_6}{\underset{|}{\overset{|}{Si}}}}-R_{3'},$$

wherein:

R_1 is a group selected from $-O-$; $-\underset{R_9}{\overset{R_8}{\underset{|}{\overset{|}{Si}}}}-O-$; or $-\underset{R_{11}}{\overset{R_{10}}{\underset{|}{\overset{|}{Si}}}}-O-\underset{R_{13}}{\overset{R_{12}}{\underset{|}{\overset{|}{Si}}}}-O-$;

R_3 and $R_{3'}$ each is a group selected from

$$CH_2=C-\underset{C_mH_{2m+1}}{\underset{|}{}}\!\!\!\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-;\ \text{or}\ CH_2=CH-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-;$$

m being a positive integer from 1 to 3;

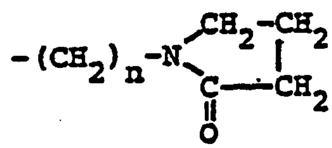
R_4 through R_{13}, inclusive, each is a group selected from

C_nH_{2n+1}; $-C_6H_5$; or $\left[-O-Si-(CH_2)\right]_n-R_{14}$;

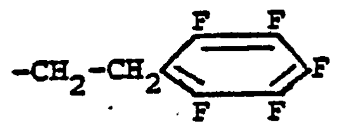
R_{14} is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$ or

$\left[-O-Si-(CH_2)_2\right]_n-R_{15}$

R_{15} is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$;

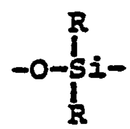


or



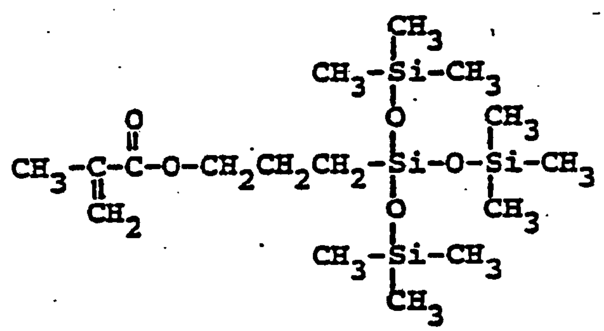
;

wherein when any of R_4 through R_{13} is other than $-CH_3$, then the substituents R on adjacent siloxane groups,

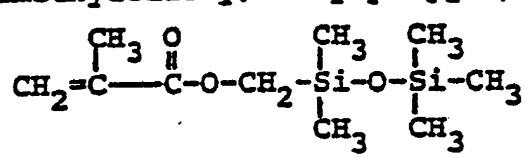


are $-C_nH_{2n+1}$ or $-C_6H_5$ and wherein n is a positive integer from 1 to 3.

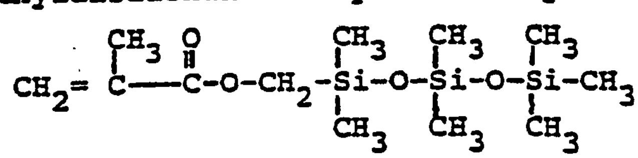
Representative silicone monomethacrylates include:



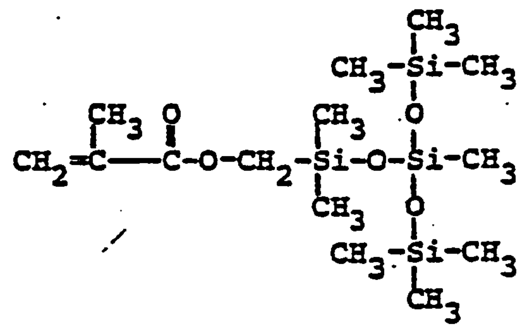
tris (trimethylsiloxy) silylpropyl methacrylate



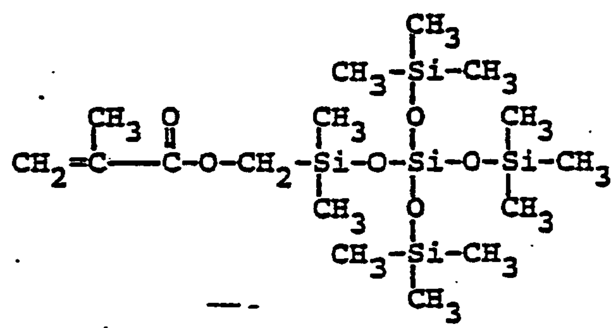
penta methyldisiloxane methyl methacrylate



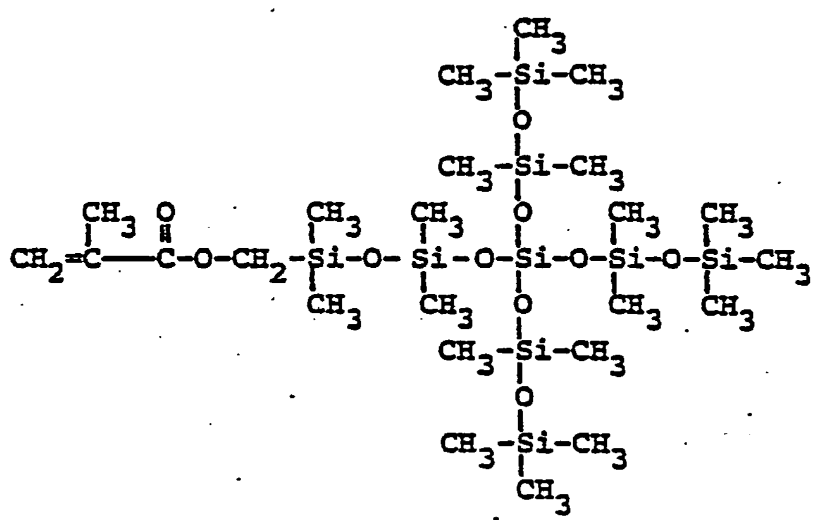
heptamethyltrisiloxanemethyl methacrylate



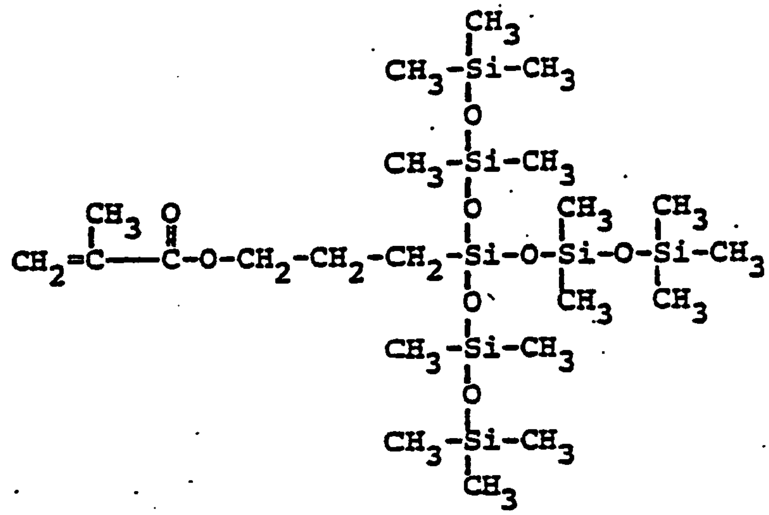
hexamethyl (trimethylsiloxy) trisiloxane methyl methacrylate



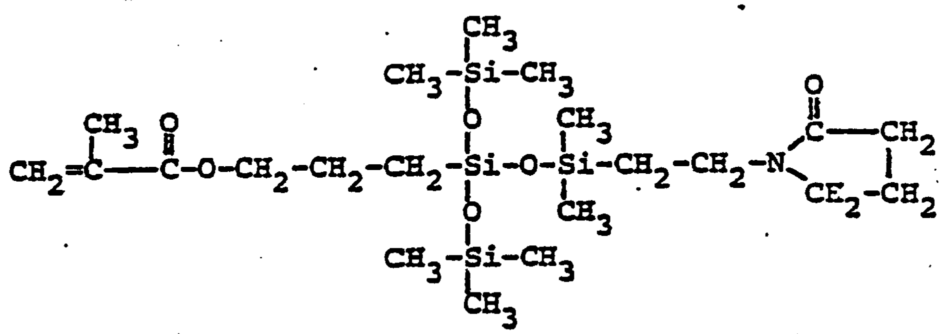
pentamethyl-bis (trimethylsiloxy) trisiloxane methyl methacrylate



nonamethyl-bis (pentamethyldisiloxanyl) pentasiloxanemethyl methacrylate

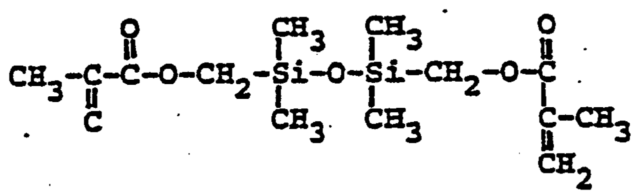


tris (pentamethyldisiloxanyl) silylpropyl methacrylate

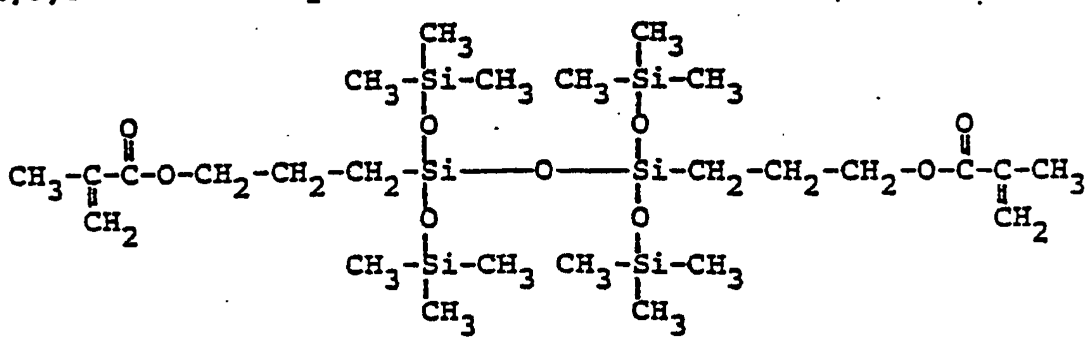


pyrrolidinonylethyldimethyl siloxy-bis (trimethylsiloxy) silylpropyl methacrylate.

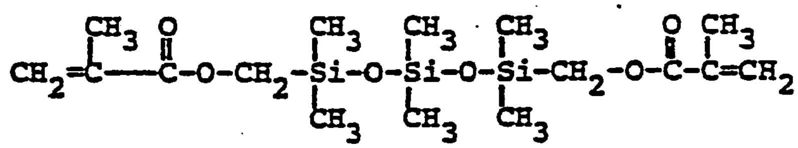
Exemplary silicone diacrylates and dimethacrylates include:



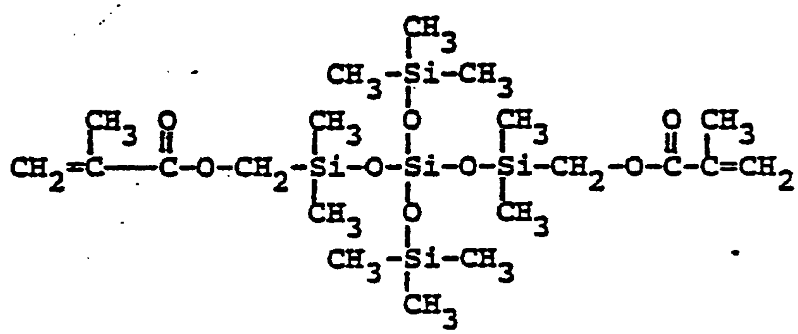
1,3 - Bis-methacryloxy methyl
1,1,3,3 - tetramethyl disiloxane



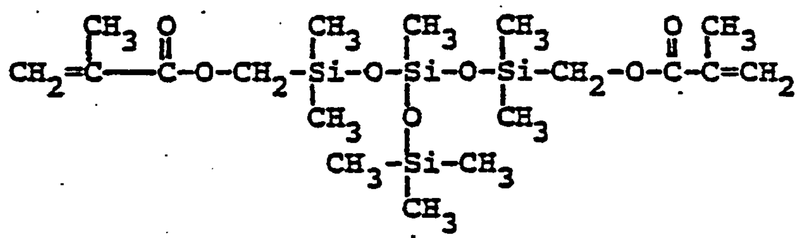
1, 3 Bis - methacryloxypropyl -
1,1,3,3 - tetrakis (trimethylsiloxy) disiloxane



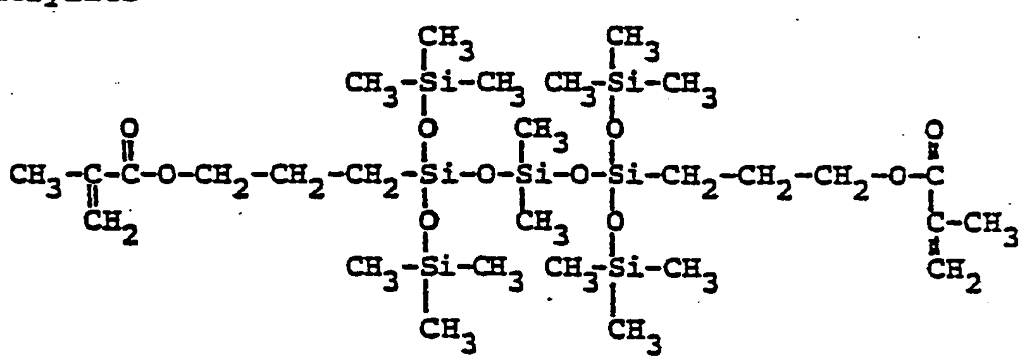
hexamethyltrisiloxane-bis (methyl methacrylate)



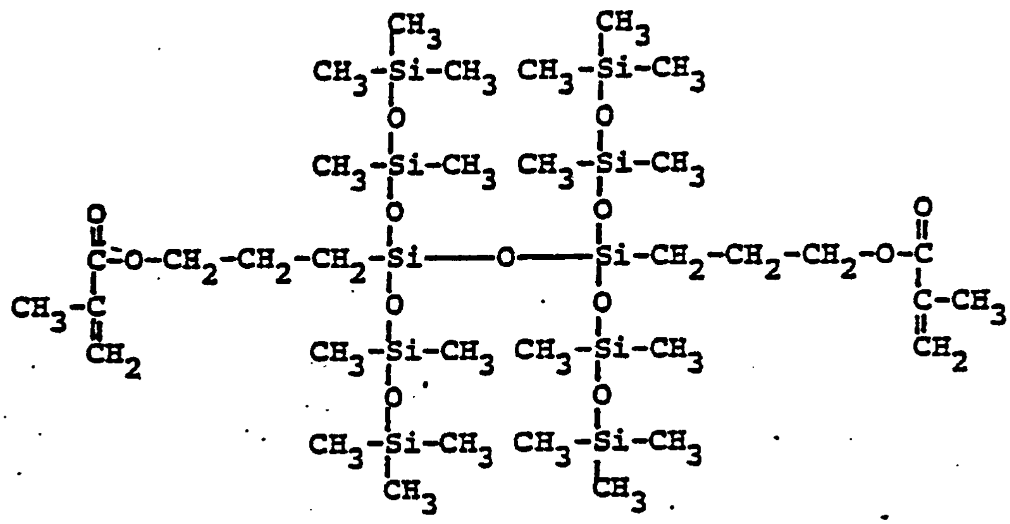
tetramethyl-bis (trimethylsiloxy) trisiloxane-bis (methyl methacrylate)



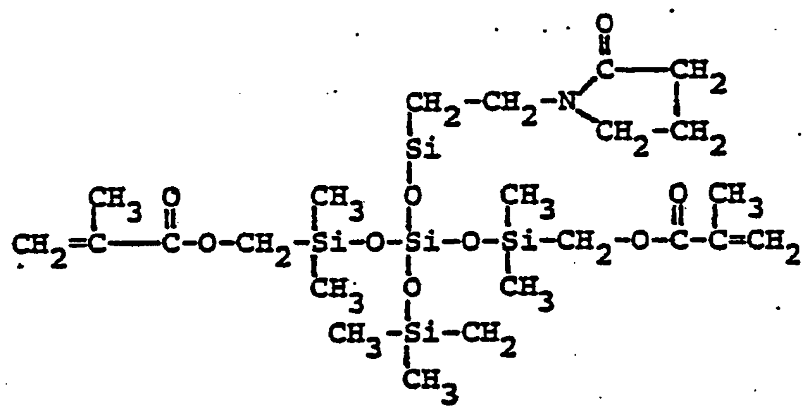
pentamethyl (trimethylsiloxy) trisilane-bis dimethyl methacrylate



1,5 Bis - methacryloxy propyl
1,1,5,5 - tetrakis (trimethylsiloxy)
3,3 - dimethyltrisiloxane



1,3 Bis - methacryloxypropyl 1,1,3,3 - tetrakis (pentamethyldisiloxanyl) disiloxane



tetramethyl-trimethylsiloxy-pyrrolidinonyldimethylsiloxy-trisiloxane-bis (methyl methacrylate)

The Preferred Embodiments

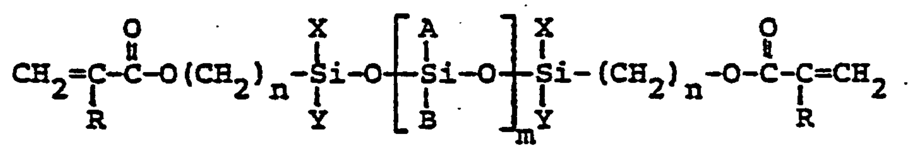
Silicone dimethacrylate (diacrylate) sters, which are new to the art, have been copolymerized with specific hydrophilic monomers to give hydrogels with excellent optical properties in the hydrated state.

The hydration level of these hydrogels may be adjusted over a wide range, by incorporating silicone methacrylate esters in the hydrogel formulation. A wide variety of lens types and prescriptions may be fabricated, which has not been possible with previous hydrogel formulations.

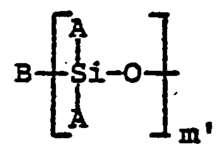
A further advantage of these formulations lies in the fact that they combine high oxygen permeability with good wetting.

As with the siloxane methacrylate esters, the oxygen permeability of the silicone dimethacrylate esters shows a wide variation within the group.

The silicone dimethacrylate ester monomer has the structure



where X and Y are selected from the class consisting of $C_1 - C_3$ alkyl groups, phenyl groups, pentafluorophenyl groups, pyrrolidinonylethyl groups, pyrrolidinonylpropyl groups and Z groups; Z is a group of the structure



A and B are selected from the class consisting of $C_1 - C_3$ alkyl groups, phenyl groups, pentafluorophenyl groups, pyrrolidinonyl ethyl groups, pyrrolidinonyl propyl groups. R is selected from the class consisting of methyl groups and hydrogen. m is an integer from zero to five; m' is an integer from one to five; n is an integer from one to three.

One embodiment f the invention provides an optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 75 percent of tris (trimethylsiloxy) silylpropyl metacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis-(trimethylsiloxy)-disiloxane or mixtures thereof;

(b) from 10 to 55 percent of vinyl pyrrolidinone or alkoxy methacrylate or mixtures thereof; and

(c) optionally up to about 30 percent pentafluorostyrene; and

(d) optionally up to about 30 percent methyl methacrylate.

Another embodiment of the invention provides an optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 75 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis (trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1;

(b) from 3 percent to 30 percent of alkoxy methacrylate; and

(c) optionally up to 55 percent of vinyl pyrrolidinone.

A further optical contact lens according to this invention has clarity, wettability and machinability and superior oxygen permeability and consists essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 30 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis-(trimethylsiloxy)-disiloxane, or mixtures thereof; and

(b) from 20 percent to 60 percent of vinyl pyrrolidinone.

The invention also provides an optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 85 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis-(trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1; and

(b) from 10 percent to 25 percent of pentafluorostyrene.

In another embodiment there is provided an optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 85 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl 1-1, 1, 3, 3-tetrakis (trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1;

(b) optionally up to 10 percent of alkoxy methacrylate;

(c) optionally up to 30 percent of vinyl pyrrolidinone; and

(d) from 10 percent to 25 percent of pentafluorostyrene.

Exampl 1

1, 5 Bis (methacryloxypropyl) 1, 1, 5, 5-tetrakis (trimethylsiloxy) 3, 3-dimethyl trisiloxane	18.00g
N-vinyl pyrrolidinone	13.00g
Methacrylic Acid	0.20g
Neozapon FLE (BASF)* (as a colorant)	0.01g
2, 2'Azobis - (2, 4-dimethyl - 4-methoxyvaleronitrile (VAZO 52)	0.03g
Tert. Butyl peroctoate (Esperox 28M, Whitco Chemical Co.)	1 drop

The above were thoroughly mixed, placed in molds and cured at 79°C for five hours. The lens blanks were hard and clear with an equilibrium hydration level of 13.7%.

*Badische Analin & Sodofabrik trademark for copper phthalacyonine dye

Example 2

1, 5 Bis (methacryloxy propyl) 1,1,5,5 - tetrakis (trimethylsiloxy) 3,5 - dimethyl-trisiloxane	15.00g
N-vinyl pyrrolidinone	25.00g
Methacrylic Acid	0.30g
Neozapon FLE (BASF)	0.01g
2, 2'Azobis-(2, 4-dimethyl - 4-methoxyraleronitrile)	0.02g
Tert. Butyl peroctoate	1 drop

The above were thoroughly mixed, placed in molds and cured at 80°C for twenty-four hours. The blanks were opaque, and not suitable for lenses.

Example 3

Tris (trimethylsiloxy) silylpropyl Methacrylate	9.00g
1, 5 - Bis (methacryloxy propyl) - 1, 1', 5, 5' - tetrakis (trimethylsiloxy) - 3, 3' - dimethyl-trisiloxane	1.00g
N-vinyl pyrrolidinone	11.10g
Methacrylic Acid	1.00g
USP 245	2 drops

The above were thoroughly mixed and then cured at 86°C for sixteen hours. The lens blanks were hard and clear, machined and polished very well. The equilibrium hydration level was 23.5%.

Example 4

Tris (trimethylsiloxy) silyl propyl Methacrylate	5.00g
1, 5 - Bis (methacryloxypropyl) 1, 1', 5, 5' - tetrakis (trimethylsiloxy) 3,3-dimethyl-trisiloxane	5.00g
N-vinyl Pyrrolidinone	11.00g
Methacrylic Acid	1.00g
USP 245 (2, 5-dimethyl-2, 5-bis (2-ethyl hexoyl) peroxide hexane)	3 drops

The above were thoroughly mixed and then cured at 84-86.5°C for eighteen hours. The lens blanks were hard and clear, machined and polished very well. The equilibrium hydration level was 17.4%.

Example 5

Tris (trimethylsiloxy) silylpropyl Methacrylate	9.00g
1, 5 - Bis (methacryloxypropyl) - 1, 1', 5, 5' - tetrakis (trimethylsiloxy) - 3, 3' - dimethyl-trisiloxane	1.00g
N-vinyl Pyrrolidinone	11.03g
USP 245	1 drop

The above were thoroughly mixed. Half of the mixture was set aside as a stock solution, the other half was cured at 84-86.5°C for thirteen hours. The lens blanks were hard and clear, machined and polished well. The equilibrium hydration level was 21.8%.

Example 6

The stock solution from example 5	10.13g
2-Hydroxyethyl Methacrylate	2.00g

The above were thoroughly mixed and cured at 84-86.5°C for thirteen hours. The lens blanks were hard and clear, machined and polished well. The equilibrium hydration level was 30.0%, the oxygen permeability was very high.

Example 7

1, 3 - Bis-methacryloxypropyl - 1, 1, 3, 3 - tetrakis (trimethylsiloxy) disiloxane	210.00g
Tris (trimethylsiloxy) silyl - propyl Methacrylate	180.00g
N-vinyl Pyrrolidinone	120.00g
2-Methoxyethyl Methacrylate	60.00g
2-Hydroxyethyl Methacrylate	24.00g
Methacrylic Acid	6.00g
Neozapon Blue FLE	0.15g
VAZO 52	0.50g

The abov wer mixed thoroughly and cured at 75°C for seven hours, to give lens blanks with good hardness and machinability. Lenses produced from these lens blanks had excellent wetting and exceptional oxygen permeability, DK = 28.5 x 10^{-11} at 20°C; see Irving Fatt and Roger St. Helen, "Oxygen Tension Under an Oxygen Permeable Contact Lens," American Journal of Optometry 1971, No. 7, p. 545 for dimensions and method of determing DK value.

Example 8

1, 3 - Bis-methacryloxypropyl - 1, 1, 3, 3-tetrakis (trimethylsiloxy) - disiloxane	7.00g
Tris (trimethylsiloxy) silyl - propyl Methacrylate	6.00g
N-(2-Methacryloxyethyl) Pyrrolidinone	4.00g
2-Methoxyethyl Methacrylate	2.00g
2-Hydroxyethyl Methacrylate	0.80g
Methacrylic Acid	0.20g
VAZO 52	0.10g

The above were mixed thoroughly and cured at 70-73°C for twenty and one-half hours to give lens blanks with good hardness and machinability. Lenses made from these lens blanks had exceptional oxygen permeability and excellent wetting.

Example 9

1, 3 Bis-methacryloxypropyl 1, 1', 3, 3'-tetrakis (trimethylsiloxy) disiloxane	0.30g
Tris (trimethylsiloxy) silyl-propyl methacrylate	7.00g
N-vinyl Pyrrolidinone	13.00g
VAZO 52	0.05g

The above were mixed thoroughly and cured at 70-115°C for one hour and fifteen minutes to give a blank which was opaque.

Example 10

1, 3 Bis-methacryloxypropyl 1,1,3, 3-tetrakis-(trimethylsiloxy) disiloxane	10.00g
Pyrrolidinonyl-2-ethyl-dimethylsiloxy-bis-(trimethylsiloxy) silyl propyl Methacrylate	5.17g
Pentafluorostyrene	5.05g
VAZO 52	0.05g

The above were mixed thoroughly and cured for six hours from 77-91°C to give lens blanks with good hardness and machinability. Lenses made from these lens blanks had exceptional oxygen permeability and good wetting.

Example 11

1, 3 Bis-methacryloxypropyl 1,1,3, 3-tetrakis (trimethylsiloxy) - disiloxane	40.00g
Tris (trimethylsiloxy) silyl - propyl Methacrylate	35.00g
N-vinyl Pyrrolidinone	25.00g
Neozapon Blue FLE	0.02g
VAZO 52	0.10g

The above were thoroughly mixed and cured at 75°C for seven and one-half hours to give lens blanks with good hardness and machinability. Lenses produced from these lens blanks had exceptional oxygen permeability and excellent wetting.

Example 12

1, 3 - Bis-methacryloxypropyl 1,1,3, 3-tetrakis (trimethylsiloxy) disiloxane	10.00g
Tris (trimethylsiloxy) silyl-propyl Methacrylate	5.00g
Pentafluorostyrene	5.05g
VAZO 52 (2, 2' Azobis (2, 4-dimethylvaleronitrile)	0.04g

The above were mixed thoroughly and cured for three and one-half hours at 73-74°C to give lens blanks with good hardness and machinability. Lenses made from these lens blanks had exceptional oxygen permeability and good wetting.

Example 13

1, 3 Bis-methacryloxypropyl 1,1,3, 3-tetrakis (trimethylsiloxy) - disoloxane	6.00g
Tris (trimethylsiloxy) silyl - propyl Methacrylate	7.00g
N-vinyl Pyrrolidinone	5.00g
Pentafluorostyrene	2.00g
VAZO 52	0.09g

The above were thoroughly mixed and cured at 72-74°C for four hours, to give lens blanks with good hardness and machinability. Lenses made from these lens blanks had exceptional oxygen permeability and excellent wetting.

Example 14

1, 3 Bis-methacryloxypropyl - 1,1,3, 3-tetrakis (trimethylsiloxy) - disiloxane	65.00g
N-vinyl Pyrrolidinone	20.00g
2-Methoxyethyl Methacrylate	10.00g
2-Hydroxyethyl Methacrylate	4.00g
Methacrylic Acid	1.00g
Neozapon Blue FLE	0.02g
VAZO 52	0.04g

The above were mixed thoroughly and cured for six hours at 74-76°C, to give lens blanks with good hardness and fair machinability. Lenses made from these lens blanks had exceptional oxygen permeability and excellent wetting but were somewhat brittle.

Example 15

1, 3 Bis-methacryloxypropyl - 1,1,3, 3-tetrakis (trimethyl - siloxy) disiloxane	11.00g
N-vinyl Pyrrolidinone	4.00g
Pentafluorostyrene	3.00g
2-Hydroxyethyl Methacrylate	2.00g
VAZO 52	0.06g

The above were thoroughly mixed, dried over $MgSO_4$, filtered and cured at 60-90°C for three hours to give lens blanks with good wetting and superior oxygen transmissibility.

Example 16

1, 3 Bis-methacryloxypropyl 1, 1', 3, 3'-tetrakis (trimethyl - siloxy) disiloxane	11.00g
N-vinyl Pyrrolidinone	6.00g
Pentaflyorostyrene	3.00g
VAZO 52	0.06g

The above were mixed thoroughly, dried over $MgSO_4$, filtered and cured at 60-90°C for two and one half hours, to give lens blanks with good wetting and superior oxygen transmissibility.

Example 17

1, 3 Bis-methacryloxypropyl - 1, 1', 3, 3'-tetrakis (trimethyl - siloxy) - disiloxane	10.00g
N-vinyl Pyrrolidinone	5.00g
Pentafluorostyrene	2.00g
VAZO 52	0.06g

The above were mixed thoroughly, dried over $MgSO_4$, filtered, and cured at 60-100°C for two and one half hours, to give lens blanks with good wetting and superior oxygen transmissibility.

Example 18

1, 3 Bis-methacryloxypropyl 1, 1', 3, 3'-tetrakis (trimethyl - siloxy) disiloxane	4.00g
Tris (trimethylsiloxy) silyl - propyl Methacrylate	9.00g
N-vinyl Pyrrolidinone	5.00g
Pentafluorostyrene	2.00g
VAZO 52	0.07g

The above were mixed thoroughly and cured for four hours at 60-80°C, to give lens blanks with good wetting and superior oxygen transmissibility.

Example 19

1, 3 Bis-methacryloxypropyl - 1, 1', 3, 3'-tetrakis (trimethylsiloxy) - disiloxane	80.00g
Tris (trimethylsiloxy) silyl - propyl Methacrylate	50.00g
N-vinyl Pyrrolidinone	40.00g
2-Methoxyethyl Methacrylate	20.00g
2-Hydroxyethyl Methacrylate	8.00g
Methacrylic Acid	2.00g
Neozapon Blue FLE	0.04g
VAZO 52	0.10g

The above were thoroughly mixed, dried over $MgSO_4$, filtered and cured at 70-75°C, under N_2 for 4 to 6 hours. The lens blanks had a hardness of 74-75D and gave lenses with superior wetting and oxygen permeability.

Example 20

Tris (trimethylsiloxy) silyl propyl Methacrylate	6.00g
N-vinyl Pyrrolidinone	5.00g
2-Hydroxyethyl Methacrylate	1.00g
Ethylene Dimethacrylate	0.10g
Methacrylic Acid	0.20g
VAZO 52	0.06g

The above were mixed thoroughly and cured for nineteen hours from 60-90°C, to give lens blanks which hydrated to 44% with superior oxygen permeability.

Example 21

1, 3 Bis-methacryloxypropyl 1, 1', 3, 3'-tetrakis (trimethyl-siloxy) - disiloxane	0.30g
Tris (trimethyl siloxy), silyl propyl Methacrylate	7.00g
N-vinyl Pyrrolidinone	11.00g
2-Hydroxyethyl Methacrylate	2.00g
VAZO 52	0.05g

The above were mixed and thoroughly dried over $MgSO_4$, filtered and cured for two hours at 60-75°C, to give lens blanks with a hydration level of 52% with superior oxygen transmissibility.

Example 22

1, 3 Bis-methacryloxypropyl 1, 1', 3, 3'-tetrakis (trimethyl-siloxy)-disiloxane	0.30g
Tris (trimethylsiloxy) silyl-propyl Methacrylate	6.00g
N-vinyl Pyrrolidinone	10.00g
2-Hydroxyethyl Methacrylate	4.00g
VAZO 52	0.07g

The above were mixed thoroughly, dried over $MgSO_4$, filtered, and cured at 60-118°C for four hours, to give lens blanks with a hydration level of 58% and superior oxygen transmissibility.

Example 23

1, 3-Bis-methacryloxypropyl-1, 1', 3, 3'-tetrakis (trimethyl-siloxy)-disiloxane	0.20g
Tris (trimethylsiloxy) silyl-propyl Methacrylate	6.00g
N-vinyl Pyrrolidinone	7.08g
2-Hydroxyethyl Methacrylate	7.00g
VAZO 52	0.01g

The above were mixed thoroughly, dried over $MgSO_4$, filtered and cured at 60-75°C for four hours to give blanks which were opaque.

Example 24

1, 3-Bis-methacryloxypropyl-1, 1', 3, 3'-tetrakis (trimethyl-siloxy)-disiloxane	7.50g
N-vinyl Pyrrolidinone	5.50g
2-Hydroxyethyl Methacrylate	0.50g
Triethyleneglycol Dimethacrylate	0.11g
Methacrylic Acid	0.10g
VAZO 52	0.06g

The above were mixed thoroughly, dried over $MgSO_4$, filtered, and cured for six hours at 70-77°C. The lens blanks had a hardness of 80D and hydrated to 10%, with superior oxygen permeability.

Example 25

1, 3-Bis-methacryloxypropyl-1, 1', 3, 3'-tetrakis (trimethyl-siloxy)-disiloxane	0.30g
Tris (trimethylsiloxy) silyl propyl Methacrylate	9.00g
N-vinyl Pyrrolidinone	5.00g
Methyl Methacrylate	6.00g
VAZO 52	0.10g

The above were mixed thoroughly, and cured at 60-76°C for four and one-half hours, to give lens blanks with good wetting and superior oxygen permeability.

Example 26

1, 3-Bis-methacryloxypropyl-1, 1, 3, 3-tetrakis (pentamethyl-disiloxanyl) disiloxane	25.00g
Tris (tri-methyl siloxy) silyl-propyl Methacrylate	7.50g
N-vinyl Pyrrolidinone	12.50g
2-Methoxyethyl Methacrylate	2.50g
2-Hydroxyethyl Methacrylate	2.00g
Methacrylic Acid	0.50g
VAZO 52	0.16g

The above were thoroughly mixed, then degassed under vacuum and repressured to atmospheric pressure with nitrogen. The formulation was cured at 75°C for seventeen hours, to give lens blanks with good hardness, exceptional oxygen permeability, good wettability, and good optical properties.

It has been found, surprisingly, that siloxane methacrylates, which are known to be hydrophobic, may be copolymerized with specific hydrophilic monomers to give hydrogels with excellent optical properties in the hydrated state.

The hydration level of these hydrogels may be adjusted over a wide range, giving hydrogels which are soft and flexible, to semi-soft and even ridged and hard. Thus, it is possible to fabricate a wide variety of lens types and prescriptions which is not possible, with other hydrogels.

A further advantage of these hydrogels is their extremely high oxygen permeability coupled with excellent wettability.

It has also been found, that while siloxane methacrylates are oxygen permeable, there is a wide variation in the oxygen permeability within this group of compounds, a fact which has not previously been reported.

In addition, siloxane methacrylates have been prepared which include hydriphilic groups, such as pyrrolidinone, within the molecule, thus enhancing wetting, while also maintaining high oxygen permeability.

The silicone methacrylate (acrylate monomers are best described by the following generalized formulae:

$$CH_2=\overset{R}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-\underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{Si}}-\left[O-\underset{\underset{A}{|}}{\overset{\overset{A}{|}}{Si}}\right]_m-B$$

where X & Y are selected from the class consisting of $C_1 - C_3$ alkyl groups, phenyl groups, pentafluorophenyl groups, and Z groups; Z is a group of the structure

$$B-\left[\underset{\underset{A}{|}}{\overset{\overset{A}{|}}{Si}}-O\right]_m-$$

where A and B are selected from the class consisting of $C_1 - C_3$ alkyl groups, phenyl groups, pentafluorophenyl groups; R is selected from the class consisting of methyl groups and hydrogen; m is a positive integer from one to five and n is a positive integer from one to three.

X, Y, and A may also be pyrrolidinonyl ethyl, pyrrolidinonyl propyl, hydroxyethyl or hydroxy-propyl, or dihydroxy propyl.

Surprisingly, there is a criticality in choosing the hydrophilic comonomer. When -2-hydroxyethyl methacrylate is used with vinyl pyrrolidinone in a ratio of more than about 1:1, (Examples 23 and 32) the resultant lens blank was opaque.

N-vinyl pyrrolidinone proved to be a more compatible hydrophilic comonomer, Examples 3-5 giving lens blanks of great clarity over a wide range of compositions.

Other comonomers may also be included in the formulation to improve hardness and machinability, of the lens blank in the dry, unhydrated state, such as pentafluorostyrene, styrene, toluene, alkyl methacrylates, such as methyl methacrylate, ether methacrylates, such as methoxyethyl methacrylate and methacrylic acid.

Crosslinking comonomers, in very small amounts, are also included in the formulation, such as ethyleneglycol dimethacrylate and triethylene glycol dimethacrylate. Others, known in the art, may also be used.

These phenomena are shown in the following examples.

Example 27

Hexamethyl-3-(trimethylsiloxy) tri-siloxane methyl Methacrylate	6.00g
N-vinyl Pyrrolidinone	5.00g
2-Hydroxyethyl Methacrylate	1.00g
Ethylene Dimethacrylate	0.10g
Methacrylic Acid	0.20g
2, 2'-AZO bis (2, 4-dimethyl-valeronitrile)	0.03g

The above were thoroughly mixed and then cured at 75°C for a total of fourteen hours. The lens blanks were hard and clear, machined and polished well. The equilibrium hydration level was 43%, the oxygen permeability was very high.

Example 28

Pentamethyl-3,3'-bis (trimethyl-siloxy) tri-siloxane methyl Methacrylate	6.00g
N-Vinyl Pyrrolidinone	5.00g
2-Hydroxyethyl Methacrylate	1.00g
Ethylene Dimethacrylate	0.10g
Methacrylic Acid	0.20g
2,2'-Azobis (2,4-dimethylvaleronitrile)	0.03g

The above were thoroughly mixed and then cured at 75°C for a total of fourteen hours. The lens blanks were hard and clear, machined and polished well. The equilibrium hydration level was 41%, the oxygen permeability was very high.

Example 29

Tris (trimethylsiloxy) silyl-propyl Methacrylate	6.00g
N-Vinyl Pyrrolidinone	5.00g
2-Hydroxyethyl Methacrylate	1.00g
Ethyleneglycol Dimethacrylate	0.10g
Methacrylic Acid	0.20g
2,2' Azobis (2,4-dimethylvaleronitrile)	0.06g

The above were thoroughly mixed, and cured at 60-68°C for three hours and at 85-93°C for fourteen hours, giving lens blanks which were clear and colorless, and machined and polished very well. The equilibrium hydration level was 44% and the oxygen permeability was very high.

Example 30

Tris (trimethylsiloxy) silylpropyl Methacrylate	3.00g
2-Pyrrolidinonyl ethyl-dimethyl-siloxy-bis (tri-methyl siloxy)-silylpropyl Methacrylate	3.00g
N-Vinyl Pyrrolidinone	4.00g
2-Hydroxyethyl Methacrylate	0.50g
Triethyleneglycol Dimethacrylate	0.10g
Methacrylic Acid	0.13g
2,2' Azobis (2,4-dimethylvaleronitrile)	0.05g

The above were thoroughly mixed and cured at 52-85°C for one-half hour and at 85-93°C for fourteen hours. The lens blanks were clear and colorless, they machined and polished very well. The equilibrium hydration level was 23%, the oxygen permeability was very high.

Example 31

Tris (trimethylsiloxy) silylpropyl Methacrylate	4.50g
1,5-Bis (methacryloxy propyl) 1,1,55-tetrakis (trimethylsiloxy) -3,3-dimethyl trisiloxane	0.50g
N-Vinyl pyrrolidinone	2.50g
2-Hydroxyethyl methacrylate	2.50g
2,5-Dimethyl-2,5-bis (2-ethyl hexoyl) peroxyl hexane	1 drop

The above were thoroughly mixed, placed in molds, and cured for nineteen hours at 99-100°C. The lens blanks were clear and colorless.

Example 32

Tris (tri-methylsiloxy) silylpropyl Methacrylate	4.50g
1,5-Bis (methacryloxy propyl) 1,1,5,5-tetrakis-(trimethylsiloxy) -3,3-dimethyl tri-siloxane	0.50g
N-Vinyl pyrrolidinone	2.00g
2-Hydroxyethyl methacrylate	3.00g
2,5-Dimethyl-2,5-bis (2-ethylhexoyl-peroxy) hexane	1 drop

The above were mixed thoroughly placed in molds in the oven and cured eighteen hours at 98-100°C. The blanks were opaque.

Example 33

Tris (trimethylsiloxy) silylpropyl Methacrylate	4.00g
1,5 Bis (methacryloxy propyl)-1,1,5,5-tetrakis (trimethylsiloxy)-3,3-dimethyl trisiloxane	0.50g
N-Vinyl pyrrolidinone	2.50g
2-Hydroxyethyl Methacrylate	3.00g
2,5-Dimethyl-2,5-Bis (2-ethylhexoyl) peroxyl hexane (U.S.P245 Witco Chem. Co.)	1 drop

The above were thoroughly mixed, placed in molds, and cured at 99-100°C for seventeen hours. The lens blanks were hard, clear, and colorless.

The preceding examples and specific compositions and methods which have been disclosed demonstrate the general nature of the invention and a number of independently significant and unpredictable facets of the invention.

In general, hydrophylic monomers which can be reacted with siloxanes of the type described to form either mono- or di-acrylate and methacrylate capped comonomers are suitable for use in this invention. Examples of such capping monomers include the following methacrylates:

Glyceryl Mono-Methacrylate

$$HOCH_2\underset{OH}{CH}-CH_2-O\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

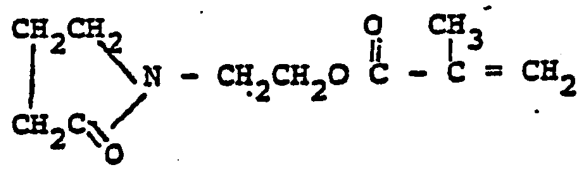
Diethyleneglycol Mono Methacrylate

$$HOCH_2CH_2OCH_2CH_2O\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

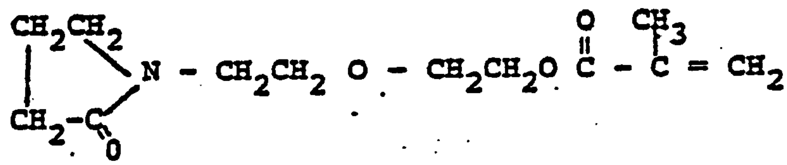
Triethyleneglycol Mono Methacrylate

$$HOCH_2CH_2OCH_2CH_2OCH_2CH_2O\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

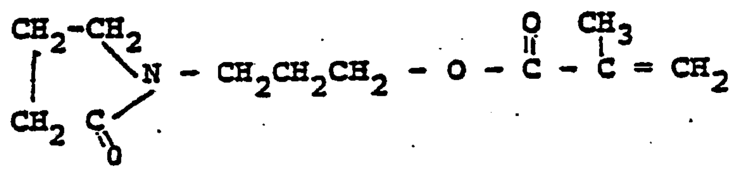
2-N-Pyrrolidinonylethyl Methacrylate



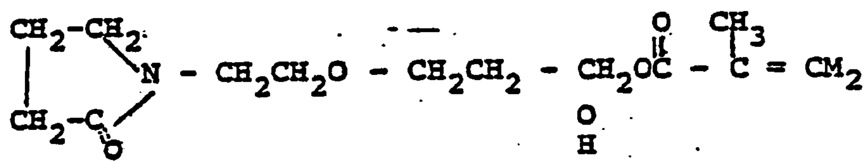
2-N-Pyrrolidinonylethoxyethyl Methacrylate

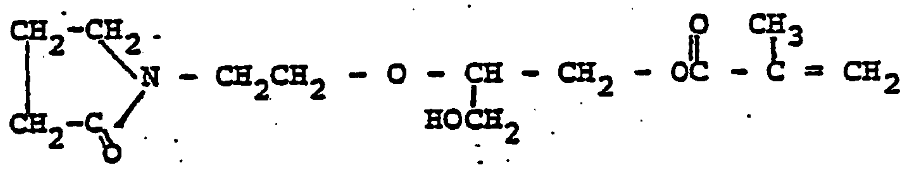


3-N-Pyrrolidinonylpropyl Methacrylate

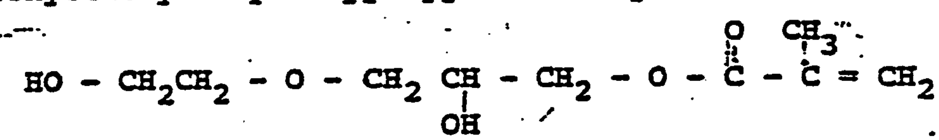


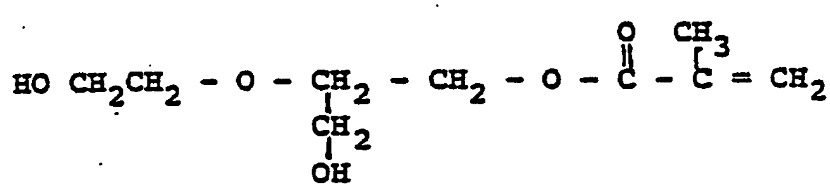
3 (2-N-Pyrrolidinonylethoxy)-2-hydroxypropyl Methacrylate



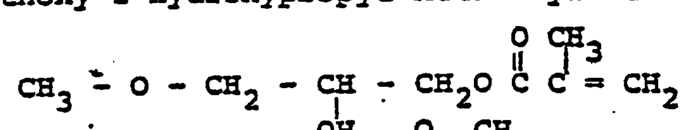


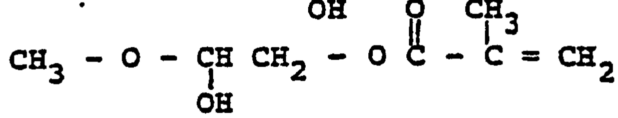
Hydroxyethoxy-2-Hydroxypropyl Methacrylate



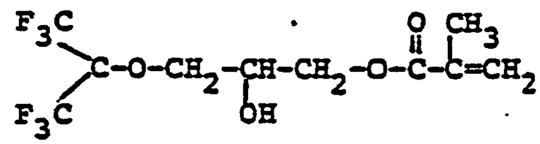


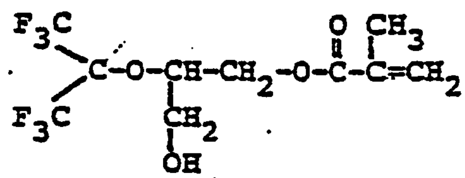
3-Methoxy-2-Hydroxypropyl Methacrylate



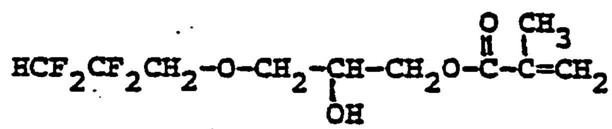


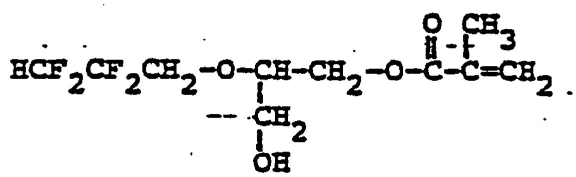
3-Hexafluoroisopropoxy-2-Hydroxy-propyl Methacrylate



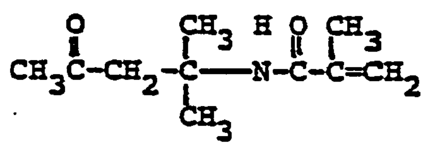


1H, 1H, 3H tetrafluoropropoxy-2 Hydroxy-propyl Methacrylate





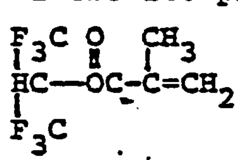
Diacetone Methacrylamide



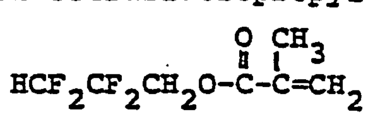
Any monomer which is reactive to form capped siloxanes may be considered for use in this invention, such as the acrylates which are analogous to the above methacrylates and the hydrophylic monomers referred to in the discussion of the prior art hereinbefore.

Other comonomers include, in addition to those previously discussed, the following methacrylates and analogous acrylates:

Hexafluoro-iso-propyl Methacrylate



1H, 1H, 3H-tetrafluoropropyl Methacrylate



1H,1H,5H-Octaflu r pentyl Methacrylate

$$HCF_2CF_2CF_2CF_2CH_2O\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

1H,1H,7H-Dodecafluoroheptyl Methacrylate

$$HCF_2CF_2CF_2CF_2CF_2CF_2CH_2O\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

1H,1H-Heptafluorobutyl Methacrylate

$$CF_3CF_2CF_2-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

TABLE I

SUMMARY OF EXAMPLES

No.	Lens Polymer Composition						Lens Polymer Characteristics				
	Mono-acrylate	Di* acrylate	VP*	HEMA*	PFS*	MAA & Other	Optical Quality	Hardness "D" Scale	Hydration % H_2O	Machin-ability	Oxygen Permeability
1	–	42	57	–	–	MAA-6	Clear	A	14%	Good	S
2	–	37	62	–	–	MAA-8	Opaque	–	–	–	–
3	40	5	50	–	–	MAA-5	Clear	A	–	Good	S
4	23	23	50	–	–	MAA-4	"	A	17.4%	"	S
5	43	5	52	–	–	–	"	A	21.8%	"	S
6	37	4	45	16	–	–	"	A	30%	"	S
7	30	35	20	14	–	MAA-1	"	A	$W^{(2)}$	"	S
8	30	35	20	14	–	MAA-1	"	A	"	"	S
9	35	1	64	–	–	–	Opaque	–	–	–	–
10	25	50	(1)	–	25	–	Clear	A	W	Good	S
11	35	40	25	–	–	–	"	A	"	"	S
12	25	50	–	–	25	–	"	A	"	"	S
13	35	30	25	–	10	–	"	A	"	"	S
14	–	65	20	14	–	MAA-1	"	Brittle	"	Fair	S
15	–	55	20	10	15	–	"	A	"	Good	S
16	–	55	30	–	15	–	"	A	"	"	S
17	–	59	30	–	11	–	"	A	"	"	S
18	45	20	25	–	10	–	"	A	"	"	S

Table I - Continued

No.	Lens Polymer Composition						Lens Polymer Characteristics				
	Mono-acrylate	Di* acrylate	VP*	HEMA*	PFS*	MAA & Other	Optical Quality	Hardness "D" Scale	Hydration % H_2O	Machin-ability	Oxygen Permeability
19	25	40	20	14	-	MAA-1	Clear	A	W	Good	S
20	49	40	8	-	-	2,1 (2)	"	A	44%	"	S
21	35	1	54	10	-	-	"	A	52%	"	S
22	30	1	49	20	-	-	"	A	58%	"	S
23	30	1	35	34	-	-	Opaque	-	-	-	-
24	0	55	40	3	-	1,1 (3)	Clear	80D	10%	Good	S
25	44	1	25	-	-	MAA-29	"	Good	W	"	S
26	15	50	25	9	-	MAA-1	"	A	"	"	S
27	49	-	41	8	-	2,1 (2)	"	A	43%	"	A
28	49	-	41	8	-	2,1 (2)	"	A	41%	"	A
29	49	-	41	8	-	2,1 (2)	"	A	44%	"	A
30	56	-	37	5	-	1,1 (3)	"	A	23%	"	A
31	45	5	25	25	-	-	"	A	W	"	S
32	45	5	20	30	-	-	Opaque	-	-	-	-
33	40	5	25	30	-	-	Clear	Good	W	Good	S
34**	15	1.5	50	35	-	-	"	84	52%	"	S
35**	30	1	35	35	-	-	Opaque	82	-	-	-
36**	25	1.5	46	30	-	-	Clear	82	57%	Good	S
37**	30	1.5	50	20	-	-	"	83	58%	"	S
38**	35	1.5	55	10	-	-	"	83	56	"	S

Table I - Continued

No.	Lens Polymer Composition						Lens Polymer Characteristics				
	Mono-acrylate	Di* acrylate	VP*	HEMA*	PFS*	MAA & Other	Optical Quality	Hardness "D" Scale	Hydration % H_2O	Machin-ability	Oxygen Permeability
39**	35	1.5	65	-	-	-	Opaque	-	-	-	-
40**	30	1.5	65	5	-	-	Clear	A	W	Good	S
41**	12	53	20	14	-	MAA-1	Clear	A	W	Good	S
42**	15	50	20	-	15	-	"	A	W	"	S
43**	25	50	-	-	25	-	"	A	W	"	S
44**	15	50	25	-	10	-	"	A	W	"	S
45**	-	55	30	-	15	-	"	A	W	"	S
46**	-	55	20	10	15	-	"	A	W	"	S
47**	15	55	20	-	10	-	"	A	W	"	S
48**	45	20	25	-	10	-	"	A	W	"	S
49**	35	30	25	-	10	-	"	76	W	"	S
50**	45	1.5	25	-	-	MAA-30	"	"	W	"	S
51**	35	40	25	-	-	-	"	"	W	"	S
52**	30	35	20	14	-	MAA-1	"	"	W	"	S

* Compounds listed by class, and percentages, by weight, rounded and approximated, see the description of the example for exact compound and amounts.

**These examples were carried out in the manner described and exemplified using the weight percentages stated, but are not separately reported here.

VP = vinyl pyrrolidinone (or equivalent derivative thereof;
HEMA = 2-hydroxyethyl methacrylate (or equivalent hydroxyalkyl acrylate or methacrylate)
PFS = pentafluorostyrene (or equivalent fluoro compound with a carbon-carbon double bond)
MA = methacrylic acid
MMA = methyl methacrylate

A=Acceptable
W=Good wettability
A=Superior

NOTES: (1) Vinyl pyrrolidinonyl moeity attached to siloxane diacrylate comonomer
(2) MAA and ethylene dimethacrylate
(3) MAA and triethyleneglycol dimethacrylate

Discoveries and Unexpected Results

A number of n w characteristics, features and results which could not have been foreseen or predicted from the known lenses, lens materials and lens technology.

It was discovered, for example, that there was a very striking difference in oxygen permeability, both as to permeability constant and rate of attainment of equilibrium of oxygen transmission when mono- and di-acrylate or methacrylate siloxanes were used as comonomers to form the ultimate lens polymer. Oxygen permeability, at equilibrium, of such lens polymers, e.g. those in all but examples Nos. 27-30, was significantly higher monoacrylate siloxane lens polymers, by a factor of three or more in most instances. For example, the oxygen permeability of the lens polymer of Example 7 has a DK value of 28.5×10^{-11}, using the procedure and nomenclature of Fatt and St. Helen, "Oxygen Tension Under an Oxygen-Permeable Contact Lens", American Journal of Optometry, 1971, No. 7, pp. 545-555, whereas lens polymers described in the prior art Gaylord U.S. Patent No. 3,808,178 have a DK value of only 4×10^{-11}, obtained by converting values in said patent to DK values). Of equal or even greater importance to the user, or equilibrium in oxygen permeability of the mono- and di- acrylate siloxane lens polymers of this invention is reach very much more rapidly, when the lens is removed from wash or storage liquid and placed in use. This unexpected phenomenon, which cannot yet be explained, is of especial importance for long term users of contact lenses. Prior art lenses often depleted the oxygen at the eye such that when equilibrium was finally reached the eye surface tissues had sustained damage or irritation from which it would not recover during the period the lens is to be worn. Using the aforementioned lens polymers of this invention, no such injury results thus permitting many to wear long

term lenses who might not otherwise be able to do so, making the wearing of long term lenses more comfortable for all users. By way of example, though there is some variability between particular materials, the aforementioned lens polymers of this invention pass substantial amounts of oxygen through lenses formed thereof within as little as 30 seconds whereas the best prior art lenses, now known to applicant, require 3 to 4 minutes before any significant amount of oxygen reached the other side of lenses.

It was also a surprise to discover that there is a relatively critical ratio of vinyl pyrrolidinone and hydroxyalkyl methacrylate which can be copolymerized with the siloxane methacrylate polymer system of this invention. It was found, for example, that the ratio of hydroxyalkyl methacrylate to vinyl pyrrolidinone must not exceed more than about 1:1. Any proportion significantly in excess of this ratio results in an opaque material unsuitable for use as a lens polymer. As shown by the examples, the ratio may be just slightly greater than 1:1 but significantly higher ratios must be avoided.

Related to the previous discussion of oxygen permeability, it was discovered that, contrary to what one would predict, the inclusion of siloxane diacrylate and siloxane dimethacrylate does not diminish oxygen permeability in a siloxane based or containing polymer system. Extrapolating from known permeability, one would predict a significant reduction in oxygen permeability of dimethacrylate siloxanes as compared with monomethacrylate siloxanes. While the use of dimethacrylate siloxanes might be expected to increase dry hardness of the lens polymer, one would not expect to increase oxygen permeability as well. It was found, however, that dimethacrylate siloxane based lens polymers were more

xygen permeable, by a very substantial factor, than monomethacrylate lens polymers, and that the inclusion of even small amounts, e.g. greater than about one weight percent, of the dimethacrylate siloxane greatly improved oxygen permeability.

In general, harder lenses are formed with higher amounts of siloxane dimethacrylate or siloxane diacrylate, as compared with monomethacrylates or monoacrylates.

Vinyl pyrrolidinone and hydroxyalkyl methacrylates when copolymerized into the lens polymers increase wettability and level of hydration, and increase dry hardness of the lens, improving machinability and general physical characteristics for forming lenses; however, too much of either monomer in the system results in a polymer which is opaque and not suitable for forming lenses. From about 10 percent (all percentages by weight) to about 55 to 60 percent vinyl pyrrolidinone may be copolymerized with siloxane dimethyl methacrylate (or equivalent di-acrylate capped siloxane) or with mixtures of mono- and di- methyl methacrylates (or equivalent mono- and di- acrylate capped siloxanes), the latter in a ratio of from about 1:20 to 99:1 di- to mono- acrylate siloxane.

The inclusion of a relatively small amount, e.g. as little as five percent, of hydroxyalkyl acrylate or methacrylate tends to increase the compatability of the siloxane system for vinyl pyrrolidinone.

Hydroxyalkyl methacrylates and acrylates can be tolerated, and improve wetting and hydration, in amounts of from about ten percent, to significantly improve wetting, to about forty percent. Lesser amounts can be included, of course, but with diminishing effect upon the wettability and hydratability of the lens polymer which results from polymerization of the siloxane system with hydroxyalkyl acrylates and methacrylates.

Fluorinated vinyl-group containing monomers may be included in amounts of from trace levels t about thirty percent, ten to thirty being the preferred effective range, to increase the wettability and oxygen permeability of the resulting lens polymer, following polymerization of a mixture of mono- and di- methacrylate or acrylate siloxanes, as described before, with the fluorinated vinyl compound, with or without a "wetting" monomer such as vinyl pyrrolidinone or a hydroxyalkyl methacrylate or acrylate.

For hard lenses, the ratio of monoacrylate (or methacrylates) siloxane to diacrylates (or methacrylate) siloxane should be from about 1:1 to about 2:1; whereas for soft lenses the ratio of these monomers should be 10:1 or greater.

Methacrylic acid and methylmethacrylate may also be included in the monomeric mixture before polymerization, in amounts of up to about two percent methacrylic acid and up to about thirty percent methyl methacrylate with destroying the advantages lens polymer characteristics of the subject invention. These monomers, when copolymerized into the polymers of this invention, tend to decrease oxygen permeability slightly but can be tolerated to the degree indicated and tend to improve the machinability of the resulting lens polymers.

Another great advantage which is somewhat subjective in observation but is nonetheless real and important in the practical application of the inventive concepts of this invention is that the inclusion of dimethacrylate (or diacrylate) siloxanes with monomethacrylate siloxanes or the use of dimethacrylates alone provides a very much more stable monomeric system which is easier to handle during pre-polymerization procedures, is easier to copolymerize with the other co-monomers discussed, and gives much more predictable, higher quality lens monomers.

Industrial Application

Very preliminary trials indicate that not only are lenses of the composition described above suitable for long term use, i.e., continuous wear, 24 hours a day, for weeks or months, but that, as result of wearing these lenses swelling of the cornea, which occurs with other long term lenses, is eliminated and the cornea returns to its normal non-swollen, configuration, thus establishing that the combined characteristics of wettability and oxygen permeability effectively keep the eye fed with essential oxygen during periods of wear.

This invention is useful in the manufacture of optical contact lenses and may be used in the manufacture of other optical devices.

WHAT IS CLAIMED IS:

1. A contact lens composed of a material conprising the solid polymerization product of comonomers comprising:

(a) from 5 weight percent to 99 weight percent silicone monoacrylate or methacrylate having the formula:

$$R_2-\overset{R_4}{\underset{R_5}{Si}}-R_1-\overset{R_6}{\underset{R_7}{Si}}-R_3$$

wherein:

R_1 is a group selected from $-O-$; $-\overset{R_8}{\underset{R_9}{Si}}-O-$; or $-\overset{R_{10}}{\underset{R_{11}}{Si}}-O-\overset{R_{12}}{\underset{R_{13}}{Si}}-O-$;

R_2 is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$;

R_3 is a group selected from

$$CH_2=\underset{C_mH_{2m+1}}{C}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-; \text{ or } CH_2=CH-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-;$$

m being a positive integer from 1 to 3;

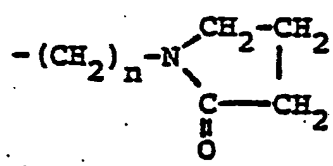
R_4 through R_{13}, inclusive, each is a group selected from

C_nH_{2n+1}; $-C_6H_5$; or $\left[-O-Si-(CH_2)\right]_n-R_{14}$;

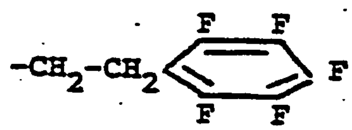
R_{14} is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$ or

$\left[-O-Si-(CH_2)_2\right]_n-R_{15}$

R_{15} is a group selected from $-C_nH_{2n+1}$; C_6H_5;



or



;

wherein when any of R_4 through R_{13} is other than $-CH_3$, then the substituents R on adjacent siloxane groups,

$$-O-\overset{R}{\underset{R}{Si}}-$$

are $-C_nH_{2n+1}$ r $-C_6H_5$ and wherein n is a positive integer from 1 to 5; and

(b) fr m 1 weight percent to 95 weight percent silicone diacrylate or dimethacrylate having the formula

$$R_3-\underset{R_5}{\overset{R_4}{\underset{|}{\overset{|}{Si}}}}-R_1-\underset{R_7}{\overset{R_6}{\underset{|}{\overset{|}{Si}}}}-R_{3'},$$

wherein

R_1 is a group selected from $-O-$; $-\underset{R_9}{\overset{R_8}{\underset{|}{\overset{|}{Si}}}}-O-$; or $-\underset{R_{11}}{\overset{R_{10}}{\underset{|}{\overset{|}{Si}}}}-O-\underset{R_{13}}{\overset{R_{12}}{\underset{|}{\overset{|}{Si}}}}-O-$;

R_3 and $R_{3'}$ each is a group selected from

$$CH_2=\underset{C_mH_{2m+1}}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-(CH_2)n-;\ \text{or}\ CH_2=CH-\overset{O}{\overset{\|}{C}}-O(CH_2)_n-;$$

m being a positive integer from 1 to 3;

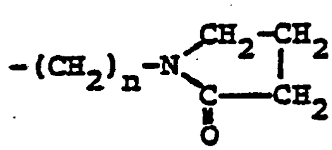
R_4 through R_{13}, inclusive, each is a group selected from

$$C_nH_{2n+1};\ -C_6H_5;\ \text{or}\ \left[-O-Si-(CH_2)\right]_n-R_{14};$$

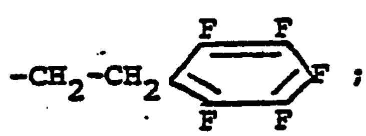
R_{14} is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$ or

$$\left[-O-Si-(CH_2)_2\right]_n-R_{15}$$

R_{15} is a group selected from $-C_nH_{2+1}$; $-C_6H_5$;



or



;

and wherein when any of R_4 through R_{13} is other than $-CH_3$, then the substituents R on adjacent siloxane groups,

$$-O-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-$$

are $-C_nH_{2n+1}$ or $-C_6H_5$

and wherein n is a positive integer from 1 to 5.

2. A contact lens as claimed in Claim 1, wherein said material results from the copolymerization of said comonomers with the inclusion of from 10 to 55 percent vinyl pyrrolidinone.

3. A contact lens as claimed in Claim 1 or 2, wherein said material results from the copolymerization of said comonomers with the inclusion of from 10 to 30 percent fluorinated vinyl compound.

4. A contact lens as claimed in Claim 3 wherein the fluorinated vinyl compound is pentafluorostyrene.

5. An optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 75 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis-(trimethylsiloxy)-disiloxane or mixtures thereof;

(b) from 10 to 55 percent of vinyl pyrrolidinone or alkoxy methacrylate or mixtures thereof; and

(c) optionally up to about 30 percent pentafluorostyrene; and

(d) optionally up to about 30 percent methyl methacrylate.

6. An optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 75 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis (trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1;

(b) from 3 percent to 30 percent of alkoxy methacrylate; and

(c) optionally up to 55 percent of vinyl pyrrolidinone.

7. An optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 30 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis-(trimethylsiloxy)-disiloxane, or mixtures thereof; and

(b) from 20 percent to 60 percent of vinyl pyrrolidinone.

8. An optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 85 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis-(trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1; and

(b) from 10 percent to 25 percent of pentafluorostyrene.

9. An optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 85 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl 1-1, 1, 3, 3-tetrakis (trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1;

(b) optionally up to 10 percent of alkoxy methacrylate;

(c) optionally up to 30 percent of vinyl pyrrolidinone; and

(d) from 10 percent to 25 percent of pentafluorostyrene.

AMENDED CLAIMS
(received by the International Bureau on 26 July 1982 (26.07.82))

10. A contact lens composed of a material comprising the solid polymerization product of comonomers comprising:

(a) from 5 weight percent to 99 weight percent silicone monoacrylate or methacrylate having the formula:

$$R_2-\underset{R_5}{\overset{R_4}{\overset{|}{\underset{|}{Si}}}}-R_1-\underset{R_7}{\overset{R_6}{\overset{|}{\underset{|}{Si}}}}-R_3$$

wherein:

R_1 is a group selected from $-O-$; $-\underset{R_9}{\overset{R_8}{\overset{|}{\underset{|}{Si}}}}-O-$; or $-\underset{R_{11}}{\overset{R_{10}}{\overset{|}{\underset{|}{Si}}}}-O-\underset{R_{13}}{\overset{R_{12}}{\overset{|}{\underset{|}{Si}}}}-O-$;

R_2 is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$;

R_3 is a group selected from

$$CH_2=\underset{C_mH_{2m+1}}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-;\ \text{or}\ CH_2=CH-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-;$$

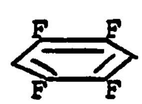
m being a positive integer from 1 to 3;

R_4 through R_{13}, inclusive, each is a group selected from

$$C_nH_{2n+1};\ -C_6H_5;\ \text{or}\ \left[-O-Si-(CH_2)\right]_n-R_{14};$$

R_{14} is a group selected from

$$-C_nH_{2n+1};\ -C_6H_5;\ \text{or}\ \left[-O-Si-(CH_2)\right]_n-R_{15};$$

R_{15} is $-CH_2-CH_2$  F;

wherein when any of R_4 through R_{13} is other than $-CH_3$, then the substituents R on adjacent siloxane groups,

$$\begin{array}{c} R \\ | \\ -O-Si- \\ | \\ R \end{array}$$

are $-C_nH_{2n+1}$ or $-C_6H_5$

and wherein n is a positive integer from 1 to 5; and

(b) from 1 weight percent to 95 weight percent silicone diacrylate or dimethacrylate having the formula

$$R_3-\underset{R_5}{\overset{R_4}{Si}}-R_1-\underset{R_7}{\overset{R_6}{Si}}-R_{3'},$$

wherein

R_1 is a group selected from $-O-$; $-\underset{R_9}{\overset{R_8}{Si}}-O-$; or $-\underset{R_{11}}{\overset{R_{10}}{Si}}-O-\underset{R_{13}}{\overset{R_{12}}{Si}}-O-$;

R_3 and $R_{3'}$ each is a group selected from

$$CH_2=\underset{C_mH_{2m+1}}{C}-\overset{O}{\overset{\|}{C}}-O-(CH_2)n-; \text{ or } CH_2=CH-\overset{O}{\overset{\|}{C}}-O(CH_2)_n-;$$

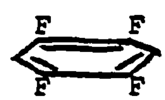
m being a poitive integer from 1 to 3;

R_4 through R_{13}, inclusive, each is a group selected from

$$C_nH_{2n+1}; \ -C_6H_5; \text{ or } \left[-O-Si-(CH_2)\right]_n-R_{14};$$

R_{14} is a group selected from $-C_nH_{2n+1}$; $-C_6H_5$ or

$$\left[-O-Si-(CH_2)_2\right]_n-R_{15}$$

R_{15} is $-CH_2-CH_2$  F;

and wherein when any of R_4 through R_{13} is other than $-CH_3$, then the substituents R on adjacent siloxane groups,

$$\begin{array}{c} R \\ | \\ -O-Si- \\ | \\ R \end{array}$$

are $-C_nH_{2n+1}$ or $-C_6H_5$

and wherein n is a positive integer from 1 to 5.

11. A contact lens as claimed in Claim 10, wherein said material results from the copolymerization of said comonomers with the inclusion of from 10 to 30 percent fluorinated vinyl compound.

12. An optical contact lens having clarity, wettability and mechinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 75 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis-(trimethylsiloxy)-disiloxane or mixtures thereof;

(b) from 10 to 55 percent of vinyl pyrrolidinone or alkoxy methacrylate or mixtures thereof; and

(c) from about 10 percent to about 30 percent pentafluorostyrene; and

(d) optionally up to about 30 percent methyl methacrylate.

13. An optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 75 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-tetrakis(trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1;

(b) from 3 percent to 30 percent of alkoxy methacrylate; and

(c) optionally up to 55 percent of vinyl pyrrolidinone.

14. An optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percnt to 85 percent of tris (trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl-1, 1, 3, 3-bis-tetrakis-(trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1; and

(b) from 10 percent to 25 percent of pentafluorostyrene.

15. An optical contact lens having clarity, wettability and machinability and having superior oxygen permeability consisting essentially of the polymerization product of the following with suitable polymerization initiators:

(a) from 15 percent to 85 percent of tris(trimethylsiloxy) silylpropyl methacrylate or 1, 3-bis-methacryloxypropyl 1-1, 1, 3, 3-tetrakis (trimethylsiloxy)-disiloxane, or mixtures thereof, in a ratio of from 1:100 to 100:1.

(b) optionally up to 10 percent of alkoxy methacrylate;

(c) optionally up to 30 percent of vinyl pyrrolidinone; and

(d) from 10 percent to 25 percent of pentafluorostyrene.

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EDITORIAL NOTE

The applicant failed to renumber the amended claims in accordance with Section 205 of the Administrative Instructions.

In the absence of any specific indication from the applicant as to the correspondence between original and amended claims, these claims are published as filed and as amended.

INTERNATIONAL SEARCH REPORT PCT/US82/00352

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL[3]/ C08F/230/08
U.S. CL/ 526/242, 526/245,526/251,526/264,526/279,351/160H

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	526/242,526/245,526/251,526/264,526/279,351/160H

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US,A, 4,182,822, PUBLISHED 08 JANUARY 1980, CHANG	2,3,5,7
X	US,A, 4,242,483, PUBLISHED 30 DECEMBER 1980 NOVICKY	2,5,7
X	US,A, 4,246,389, PUBLISHED 20 JANUARY 1981, LE BOUEF	2,5,7
X,P	US,A, 4,306,042, PUBLISHED 15 DECEMBER 1981 NEEFE	1,2,5,7

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
18 MAY 1982	28 MAY 1982
International Searching Authority [1]	**Signature of Authorized Officer [10]**
ISA/US	STANFORD M. LEVIN